

Colours in Metal Glasses, in Metallic Films and in Metallic Solutions.. II

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Colours in Metal Glasses, in Metallic Films and in Metallic Solutions.—II.

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(Abstract.)

In the first section of this paper it is pointed out that one and the same metal may cause a great variety of different colours, just as the colour of gold vapour differs from the colour of the light reflected from gold as well as from the colour of the light transmitted by gold leaf. While the ultimate cause of the colour of a metalliferous medium is to be found in the structure of the metal molecule itself, the arrangement of these molecules, according to any fixed law, causes them to affect one another's free periods in a definite manner, and thus gives rise to corresponding optical properties. The object of this paper is to discover, by means of these optical properties, the molecular arrangement (microstructure) of various metal glasses, of colloidal solutions of metal and of metallic films.

Expressions giving the refractive index and the absorption coefficient (the optical constants) of a compound medium consisting of metal (1) in small spheres (granular), and (2) in discrete molecules (amorphous), diffused through an isotropic non-dispersive transparent medium (the solvent), are next investigated in terms of the corresponding optical constants of the normal metal.

The particular formulæ which apply when the volume proportion of metal in the compound medium is small, as in the case of metal glasses and of "colloidal solutions" of metal in water, are also obtained, and it is found that while spheres of any metal, so diffused that there are many to a wave-length of light, will produce colours which vary with the refractive index of the solvent, diffused molecules of any metal produce, by transmitted light, a colour (the vapour colour) which is independent of that refractive index.

By means of these formulæ and of the optical constants of gold, silver, and copper, experimentally determined for monochromatic light of several different wave-lengths, the numerical values of the corresponding optical constant which would be possessed by diffusions of spheres and of molecules in glass, water, or vacuum, are calculated and tabulated. Defining the absorption of light of wave-length λ by any absorbing medium as being

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the logarithm of the ratio of the intensities of that light before and after traversing a unit-length of the medium, graphs are given of the calculated absorptions of these diffusions. Curves are also shown representing the absorptions of specimens of gold ruby glass, of silver stained glass, and of copper ruby glass, as measured at the National Physical Laboratory.

A comparison of these curves with the graphs for gold spheres and for gold molecules in glass, and a collation of the results with others already obtained in a previous communication,* leads to the conclusion that the colour of gold ruby glass is due primarily to the presence of small spheres of gold. The irregular blue and purple colours sometimes exhibited by gold glass are then explained by the presence of crystallites caused by the coagulation of the gold spheres. Again, when the corresponding graphs with water as solvent are compared with the absorptions of colloidal gold as measured by Ehrenhaft,† little doubt remains but that colloidal gold consists of small spheres in suspension; the blue colour produced by particles coarser than the small spheres is, as in the case of glass, due to the red light being reflected by the crystallites and so not transmitted.

The close similarity between the observed absorptions of yellow glass stained with silver, and the calculated absorptions of a diffusion of silver spheres in glass—the calculated absorptions of a diffusion of silver molecules in glass are quite different—indicates that the stained region must contain small spheres of silver. Ehrenhaft's‡ description of the nature and position of the absorption band observed in the spectrum of colloidal solutions of silver, describes so well the position of the absorption band determined by calculation for a diffusion of silver spheres (but not of silver molecules) in water, as to justify the conclusion that the bulk of the silver present in colloidal solution is in the form of small spheres: little, if any, being in true solution (*i.e.*, molecularly subdivided); and this conclusion is confirmed by the fact that the refractive index of a colloidal solution of silver, which was measured by Barus and Schneider,§ is precisely that which calculation shows to be possessed by a diffusion of silver spheres (but not of molecules) in water.

Measurements, made by Sir William Abney, of the intensities with which light of various wave-lengths is reflected from the interface between the stained and unstained regions of one of the specimens of silver glass which had belonged to Stokes, when held with the stain turned away from

* 'Phil. Trans.,' A, 1904, pp. 385 to 420.

† Felix Ehrenhaft, 'Ann. der Phys.,' vol. 11, p. 489 (1903).

‡ *Loc. cit.*, p. 507.

§ Barus and Schneider, 'Zeitschr. f. Phys. Chem.,' vol. 8, p. 278.

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the source of light, are in general accordance with the reflective powers calculated on the hypothesis that small spheres of silver are distributed throughout the stained regions, the maxima corresponding to light of wavelength about $\lambda = 0.436$ in both cases. If the silver in the glass had been molecularly subdivided the maximum would have been at about $\lambda = 0.360$. The presence of silver spheres (but not of discrete molecules of silver) throughout the stained region thus accounts for the blue reflection, in accordance with Stokes,* as well as for the amber colour of silver glass viewed by transmitted light, proving that both colours were due to suspended particles of silver.

A comparison of the observed absorptions of copper ruby glass with the calculated absorptions of copper spheres and of copper molecules diffused in glass, shows that copper ruby glass owes its colour to the presence in the glass of small spheres of metallic copper,† while some copper molecules are probably also present. Although it has thus been proved that gold and copper ruby glasses and silver glass owe their colours to diffused spheres of the metal, the metals which colour some other glasses cannot be present in the metallic form; for example, the deep blue colour of cobalt glass cannot be due to diffused metallic cobalt, which, according to calculation, would give a reddish colour by transmitted light akin to that observed by Ehrenhaft‡ in a “colloidal solution” of that metal.

The colours produced in gold, silver, and soda glasses by the radiation from the emanation from radium, give rise to the suggestion that all glasses contain free ions of metal, and it is by the discharge of these ions and the consequent reduction of the metal (so that the metal is diffused in the glass), that cathode and Becquerel rays are able to colour the glasses.

Expressions are obtained giving the absorptions and reflective powers of amorphous or granular forms of gold and silver, the specific gravity of which is any proper fraction, μ , of that of the metal in its normal state. Curves are constructed to show how the values of these expressions, and thus also the colours exhibited by transmitted and by reflected light, vary with μ .

A comparison of these calculated colour changes with those actually shown by gold and silver films, such as those deposited on glass by Faraday,§ and

* Stokes, “On the Change of Refrangibility of Light,” ‘Phil. Trans.,’ 1852; ‘Collected Papers,’ vol. 3, p. 316.

† Stokes (*loc. cit.*, vol. 4, p. 245) thought copper ruby glass was coloured by suboxide of copper, and attributed the change of colour in some specimens to suspended particles of the metal.

‡ Ehrenhaft, *loc. cit.*, p. 506.

§ Faraday, Bakerian Lecture, ‘Phil. Trans.,’ 1857.

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by Beilby,* when subjected to heat and to pressure, indicates that (a) the films as first prepared are in the amorphous or granular phase, and (b) heating diminishes the density of the film, while pressure is able to increase that density again, and finally, (c) this diminution of density is probably effected by the passage of metal from the amorphous to the granular phase, and by the growth of the larger granules at the expense of the smaller, while increase of density is accomplished by changing some of the metal from the granular to the amorphous phase.

The optical properties of Carey Lea's† so-called solutions of allotropic silver show that they consist of small spheres of silver in suspension in water. From this and other evidence it is shown that the suggestions made in the former paper‡ that Carey Lea's silver was not allotropic, but consisted of normal silver in a finely divided (but not necessarily granular) state, was almost certainly correct.

The three forms of silver discovered so long ago as 1861 by Hermann Vogel,§ were probably the amorphous, granular, and crystalline forms discussed in this paper.

The paper concludes with the suggestion that many forms of metals which have hitherto been considered to be allotropic, because possessing optical properties distinct from those belonging to the metal in its normal state, are merely cases of fine division. Thus the properties of Bolley's lead,|| of Schützenberger's¶ silver and copper, and of other alleged cases of allotropy cited by Roberts-Austen,** do not require the postulation of an allotropic molecule for their explanation.

* G. T. Beilby, Hurter Memorial Lecture, Glasgow, 1897.

† Carey Lea, 'Amer. Jour. of Science' (1889), and 'Phil. Mag.' (1891).

‡ *Loc. cit.*, p. 419.

§ Hermann Vogel, 'Pogg. Ann.', vol. 117, p. 316 (1861).

|| Cf. Roberts-Austen, 'Metallurgy,' p. 90.

¶ Schützenberger, 'Bull. Soc. Chim.', vol. 30, p. 3 (1878).

** Roberts-Austen, *loc. cit.*